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EXTENSION OF BOLTZMANN'S THEORY TO A LIQUID

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A theory for the nonequilibrium statistical mechanics of a liquid is presented. This theory consists of coupled evolution equations for the one-particle momentum distribution, and for the two-particle correlation function, and it possesses the same important properties as does Boltzmann's theory, namely the local conservation laws, the local h theorem, and the correct equilibrium solution.

1 INTRODUCTION

For a gas, the energy density is a statistical average of the kinetic energy of the particles. The pressure tensor and the energy current are also composed entirely of kinetic contributions. The important statistical function, from which all densities and currents can be calculated, is the one-particle momentum distribution. In 1872, Boltzmann¹ constructed an equation describing the irreversible evolution of the momentum distribution for a nonequilibrium gas. In this equation, irreversibility arises from the collision integral, which is a statistical representation of two-particle collisions.

For a liquid, the densities and currents contain, in addition to kinetic contributions, potential contributions as well, due to the potential of interaction between liquid particles. The statistical function which is needed, to calculate these potential contributions, is the two-particle correlation function. The Boltzmann equation does not account for interparticle correlations. Much research has been devoted to the extension of Boltzmann's theory to dense gases and to liquids. We note the work of Enskog, which is discussed by Hirschfelder, Curtiss, and Bird;² the density expansion of Bogoliubov;³ the work of Cohen,⁴⁻⁶ of Ernst, Haines, and Dorfman,⁷ and of Résibois and

DeLeener,⁸ all showing that the density expansion does not converge; and the establishment of global h theorems for certain systems by Résibois,⁹ and by Karkheck, van Beijeren, de Schepper, and Stell.¹⁰

The nature of a liquid, which is in contrast to the nature of a gas, is that a given particle is in *continuous interaction* with its neighbors. Hence the concept of collisions is not appropriate for a statistical theory of a liquid. We have recently constructed a new theory of nonequilibrium statistical mechanics for a liquid.^{11,12} In the present paper, we show that this new theory is a logical extension of Boltzmann's theory.

2 BOLTZMANN THEORY

We consider a gas of like particles, each with mass m . At a location \mathbf{r} , and time t , the one-particle probability density (the momentum distribution) is $f^{(1)}(\mathbf{r}, \mathbf{p}, t)$. Note \mathbf{r} and \mathbf{p} represent vectors. All the significant densities and currents in the gas are given by the distribution $f^{(1)}$. The particle density $\rho(\mathbf{r}, t)$, and the fluid velocity $\mathbf{v}(\mathbf{r}, t)$, are given by

$$\rho(\mathbf{r}, t) = \int f^{(1)}(\mathbf{r}, \mathbf{p}, t) d\mathbf{p}, \quad (1)$$

$$\mathbf{v}(\mathbf{r}, t) = \frac{1}{m} \int \mathbf{p} f^{(1)}(\mathbf{r}, \mathbf{p}, t) d\mathbf{p} \quad (2)$$

The energy per particle, in the local center-of-mass frame, is $\epsilon^{(1)}(\mathbf{r}, t)$, where

$$\rho(\mathbf{r}, t)\epsilon^{(1)}(\mathbf{r}, t) = \int \frac{[\mathbf{r} - m\mathbf{v}(\mathbf{r}, t)]^2}{2m} f^{(1)}(\mathbf{r}, \mathbf{p}, t) d\mathbf{p}. \quad (3)$$

The pressure tensor $P^{(1)}(\mathbf{r}, t)$, and the energy current $J^{(1)}(\mathbf{r}, t)$, are given by well-known formulas which we will not exhibit here.

The Boltzmann equation is an evolution equation for the statistical function $f^{(1)}(\mathbf{r}, \mathbf{p}, t)$. The irreversible aspect of this evolution is contained in the collision integral $C(\mathbf{r}, \mathbf{p}, t)$, which we will construct in a slightly unorthodox way. At a given \mathbf{r}, t in the gas, there are two-particle collisions in which the particle momenta \mathbf{p}, \mathbf{p}' go to $\hat{\mathbf{p}}, \hat{\mathbf{p}}'$. For a given phase-space volume element $d\hat{\mathbf{p}} d\hat{\mathbf{p}}'$, the transition rate is $\chi(\mathbf{p}, \mathbf{p}'/\hat{\mathbf{p}}, \hat{\mathbf{p}}') d\hat{\mathbf{p}} d\hat{\mathbf{p}}'$. $\chi(\mathbf{p}, \mathbf{p}'/\hat{\mathbf{p}}, \hat{\mathbf{p}}')$ is invariant under the interchange of \mathbf{p}, \mathbf{p}' with $\hat{\mathbf{p}}, \hat{\mathbf{p}}'$, and $\chi(\mathbf{p}, \mathbf{p}'/\hat{\mathbf{p}}, \hat{\mathbf{p}}')$ contains two δ -functions as factors: $\delta(\mathbf{p} + \mathbf{p}' - \hat{\mathbf{p}} - \hat{\mathbf{p}}')$, representing conservation of momentum, and $\delta(p^2 + p'^2 - \hat{p}^2 - \hat{p}'^2)$, representing conservation of energy. Because of the collisions, particle pairs are entering and leaving the pair distribution $f^{(1)}(\mathbf{r}, \mathbf{p}, t)f^{(1)}(\mathbf{r}, \mathbf{p}', t)$, and the net rate of change of this pair distribution is

$$\begin{aligned} R(\mathbf{r}, \mathbf{p}, \mathbf{p}', t) = & \iint \left[f^{(1)}(\mathbf{r}, \hat{\mathbf{p}}, t)f^{(1)}(\mathbf{r}, \hat{\mathbf{p}}', t) \right. \\ & \left. - f^{(1)}(\mathbf{r}, \mathbf{p}, t)f^{(1)}(\mathbf{r}, \mathbf{p}', t) \right] \\ & \times \chi(\mathbf{p}, \mathbf{p}'/\hat{\mathbf{p}}, \hat{\mathbf{p}}') d\hat{\mathbf{p}} d\hat{\mathbf{p}}'. \end{aligned}$$

Integration of this over $d\mathbf{p}'$ gives the collisional rate of change of $\rho(\mathbf{r}, t)f^{(1)}(\mathbf{r}, \mathbf{p}, t)$. But the collisional rate of change of $\rho(\mathbf{r}, t)$ is zero, so the corresponding rate of change of $f^{(1)}(\mathbf{r}, \mathbf{p}, t)$ is the collision integral $C(\mathbf{r}, \mathbf{p}, t)$, given by

$$\rho(\mathbf{r}, t)C(\mathbf{r}, \mathbf{p}, t) = \int R(\mathbf{r}, \mathbf{p}, \mathbf{p}', t) d\mathbf{p}'. \quad (4)$$

The transition rate χ is simply related to the collision cross section σ .

The Boltzmann equation is

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} \right) f^{(1)}(\mathbf{r}, \mathbf{p}, t) = C(\mathbf{r}, \mathbf{p}, t), \quad (5)$$

where the term in $\nabla_{\mathbf{r}}$ is the drift term (streaming term). The Boltzmann equation possesses the following three important properties.

(a) For a general material, the theory of continuum mechanics expresses, in local form, the well-known laws of conservation of mass, of linear momentum, and of energy. For a gas, where the densities and currents are given by the one-particle contributions, the Boltzmann equation yields the three local conservation laws.

(b) For a function $h(\mathbf{r}, t)$, which is the h -quantity per particle at location \mathbf{r} and time t , the local h theorem is

$$\begin{aligned} \frac{\partial \rho(\mathbf{r}, t)h(\mathbf{r}, t)}{\partial t} + \nabla_{\mathbf{r}} \cdot [\rho(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t)h(\mathbf{r}, t) \\ + I(\mathbf{r}, t)] = \Sigma(\mathbf{r}, t), \end{aligned} \quad (6)$$

where $I(\mathbf{r}, t)$ is the h current, and $\Sigma(\mathbf{r}, t)$ is the source function. $\Sigma(\mathbf{r}, t)$ is a Liapunov functional, so that $\Sigma(\mathbf{r}, t) \leq 0$, with $\Sigma(\mathbf{r}, t) = 0$ only at equilibrium. To obtain an h theorem from Boltzmann's equation, it is necessary to add some information, namely the definition of $h(\mathbf{r}, t)$. Boltzmann's definition, altered to include a factor of Planck's constant h_p , is $h^{(1)}(\mathbf{r}, t)$:

$$\rho(\mathbf{r}, t)h^{(1)}(\mathbf{r}, t) = \int f^{(1)}(\mathbf{r}, \mathbf{p}, t) \ln h_p^3 f^{(1)}(\mathbf{r}, \mathbf{p}, t) d\mathbf{p}, \quad (7)$$

where the argument of the log is dimensionless. With the definition (7), Boltzmann's equation yields the local h theorem (6).

(c) The condition $\Sigma(\mathbf{r}, t) = 0$ yields a solution for the equilibrium momentum distribution $f_0^{(1)}(\mathbf{p})$. Taking into account the known equilibrium values of ρ, \mathbf{v} , and ϵ , and eliminating ϵ in favor of the inverse

temperature β , $f_0^{(1)}(p)$ is uniquely determined to be the Boltzmann distribution:

$$f_0^{(1)}(p) = \rho(\beta/2\pi m)^{3/2} \exp[-\beta(p - mv)^2/2m]. \quad (8)$$

3. EXTENSION TO A LIQUID

We now consider a liquid of like particles, interacting through the central potential $\phi(|s|)$, where s is the vector separation between two particles. The probability density for a particle at $r - \frac{1}{2}s$ with momentum p , and simultaneously a particle at $r + \frac{1}{2}s$ with momentum p' , is $f^{(2)}(r - \frac{1}{2}s, p, r + \frac{1}{2}s, p', t)$. From this, we define the two-particle correlation function $\gamma^{(2)}$:

$$\begin{aligned} f^{(2)}(r - \tfrac{1}{2}s, p, r + \tfrac{1}{2}s, p', t) \\ = f^{(1)}(r - \tfrac{1}{2}s, p, t) f^{(1)}(r + \tfrac{1}{2}s, p', t) \\ \times \gamma^{(2)}(r - \tfrac{1}{2}s, p, r + \tfrac{1}{2}s, p', t). \end{aligned}$$

To construct a simple evolution theory including two-particle correlation effects, we will introduce two approximations, which are discussed in detail in a longer paper.¹² We assume that $f^{(1)}$ and $\gamma^{(2)}$ vary by only a small relative amount when they are translated through a distance of order or less than the correlation length, and we also neglect momentum correlations, i.e. neglect the momentum dependence of $\gamma^{(2)}$. As a result of these approximations, the theory can be based on the two-particle probability density

$$f_s^{(2)}(r, s, p, p', t) = f^{(1)}(r, p, t) f^{(1)}(r, p', t) g^{(2)}(r, s, t), \quad (9)$$

together with gradients of $f^{(1)}$ and $g^{(2)}$. Here $g^{(2)}$ is the momentum-averaged correlation function:

$$\begin{aligned} \rho^2(r, t) g^{(2)}(r, s, t) = \iint f^{(1)}(r, p, t) f^{(1)}(r, p', t) \\ \times \gamma^{(2)}(r - \tfrac{1}{2}s, p, r + \tfrac{1}{2}s, p', t) dp dp'. \end{aligned} \quad (10)$$

The function $g^{(2)}(r, s, t) - 1$ is local, i.e. it vanishes when s is greater than the correlation length, and is normalized according to

$$\rho(r, t) \int [g^{(2)}(r, s, t) - 1] ds = -1 + \alpha(r, t), \quad (11)$$

where $\alpha(r, t)$ represents density fluctuations, $\alpha(r, t)$ is positive, and $\alpha(r, t) \ll 1$ for a liquid. In many cases of liquid theory, it is not unreasonable to set $\alpha = 0$ as a first approximation. The two-particle contributions to the energy and pressure, $\epsilon^{(2)}(r, t)$ and $P^{(2)}(r, t)$ respectively, are given by

$$\epsilon^{(2)}(r, t) = \frac{1}{2} \rho(r, t) \int \phi(|s|) g^{(2)}(r, s, t) ds, \quad (12)$$

$$P^{(2)}(r, t) = -\frac{1}{2} \rho^2(r, t) \int \phi'(|s|) \frac{ss}{|s|} g^{(2)}(r, s, t) ds, \quad (13)$$

where $\phi'(|s|) = d\phi(|s|)/d|s|$. From our approximations, it follows $J^{(2)}(r, t) = 0$.

Let us next consider the irreversible aspect of the evolution of a nonequilibrium liquid. This can be described in terms of effective two-particle interactions, in which two particles interact not as an isolated pair, but as a pair immersed in a sea of background interactions. In such an effective two-particle interaction, s, p, p' goes to $\hat{s}, \hat{p}, \hat{p}'$, and for a given phase-space volume element $d\hat{p}d\hat{p}'d\hat{s}$, the transition rate is $\chi(s, p, p'/\hat{s}, \hat{p}, \hat{p}') d\hat{p}d\hat{p}'d\hat{s}$. χ is local in r, \hat{s} , and the dependence of χ on r, t is suppressed for abbreviation. Because of microscopic reversibility, $\chi(s, p, p'/\hat{s}, \hat{p}, \hat{p}')$ is invariant under the interchange of p, p' with \hat{p}, \hat{p}' . Also $\chi(s, p, p'/\hat{s}, \hat{p}, \hat{p}')$ contains two δ -functions as factors: $\delta(p + p' - \hat{p} - \hat{p}')$, representing conservation of momentum, and $\delta(\omega - \hat{\omega})$, representing conservation of the "energy of mean force," where

$$\omega(r, s, p, p', t) = \frac{p^2}{2m} + \frac{p'^2}{2m} + u^{(2)}(r, s, t). \quad (14)$$

$u^{(2)}(r, s, t)$ is the local potential of mean force in the nonequilibrium liquid.^{11,12} The important point is that, in microscopic energy conservation within the effective interactions, it is not the bare potential $\phi(|s|)$

which enters, but the potential of mean force $w^{(2)}(r, s, t)$.

Because of the interactions, particles are entering and leaving the phase-space volume around s, p, p' , and the net rate of change of $f_s^{(2)}(r, s, p, p', t)$ is

$$\begin{aligned} F^{(2)}(r, s, p, p', t) \\ = \iiint \left[f_s^{(2)}(r, \hat{s}, \hat{p}, \hat{p}', t) - f_s^{(2)}(r, s, p, p', t) \right] \\ \times \chi(s, p, p' / \hat{s}, \hat{p}, \hat{p}') d\hat{p} d\hat{p}' d\hat{s}. \end{aligned} \quad (15)$$

The corresponding rate of change of $f^{(1)}(r, p, t)$ is

$$F^{(1)}(r, p, t) = \iint F^{(2)}(r, s, p, p', t) dp' ds, \quad (16)$$

and the corresponding rate of change of the quantity $\rho^2(r, t)g^{(2)}(r, s, t)$ is

$$G^{(2)}(r, s, t) = \iint F^{(2)}(r, s, p, p', t) dp dp'. \quad (17)$$

Finally, while the energy of mean force is conserved microscopically, within each effective two-particle interaction, the total energy must be conserved macroscopically, and this gives an integral condition on χ , which can be put in the form^{11,12}

$$\int \left[\phi(|s|) - w^{(2)}(r, s, t) \right] G^{(2)}(r, s, t) ds = 0. \quad (18)$$

The extension of Boltzmann's theory to a liquid is accomplished by constructing two coupled evolution equations, one for $f^{(1)}(r, p, t)$ and one for $g^{(2)}(r, s, t)$. These equations are:

$$\left(\frac{\partial}{\partial t} + \frac{p}{m} \cdot \nabla_r + L(r, t) \cdot \nabla_p \right) f^{(1)}(r, p, t) = F^{(1)}(r, p, t) \quad (19)$$

$$\begin{aligned} \rho^2(r, t) \left(\frac{\partial}{\partial t} + v(r, t) \cdot \nabla_r + s \cdot \nabla_r v(r, t) \cdot \nabla_s \right) g^{(2)}(r, s, t) \\ = G^{(2)}(r, s, t). \end{aligned} \quad (20)$$

In (19), $L(r, t)$ is the mean force on a particle at r, t , due to interactions with the surrounding liquid particles, and is given by

$$\rho(r, t)L(r, t) = -\nabla_r \cdot P^{(2)}(r, t). \quad (21)$$

In (20), the term in ∇_r is due to the drift *together* of particle pairs, and the term in ∇_s is due to the drift *apart* of particle pairs.

The coupled equations (19) and (20) possess the same important properties as does the Boltzmann equation, as noted in (a)-(c) below.

(a) When the energy, pressure, and energy current are given by the sum of one- and two-particle contributions, then the local equations for conservation of particles, of linear momentum, and of energy follow directly from (19) and (20).

(b) To prove an h theorem, we set

$$h(r, t) = h^{(1)}(r, t) + h^{(2)}(r, t),$$

where $h^{(1)}(r, t)$ is the Boltzmann form (7), and $h^{(2)}(r, t)$ is the nonequilibrium extension of our liquid correlational entropy,^{13,14}

$$h^{(2)}(r, t) = \frac{1}{2} \rho(r, t) \int g^{(2)}(r, s, t) \ln g^{(2)}(r, s, t) ds. \quad (22)$$

As a result of our approximations, $F^{(2)}(r, t) = 0$. Then the local h theorem, equation (6), follows from the liquid evolution equations (19) and (20).

(c) The equilibrium solution, obtained by setting $\Sigma(r, t) = 0$, gives again the Boltzmann expression (8) for $f_0^{(1)}(p)$, and also gives

$$g_0^{(2)}(s) = \exp \left[-\beta w_0^{(2)}(|s|) \right], \quad (23)$$

where $w_0^{(2)}(|s|)$ is the equilibrium evaluation of the potential of mean force. This is the correct equilibrium expression for the correlation function $g_0^{(2)}(s)$.

As a final note, it has been shown that, for a near equilibrium situation, our statistical evolution theory reproduces precisely the irreversible thermodynamics of a viscous heat-conducting liquid.¹²

REFERENCES

1. L. Boltzmann, Wien. Ber. 66 (1872) 275.
2. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (Wiley, New York, 1954) §9.3.
3. N. N. Bogoliubov, in: Studies in Statistical Mechanics, Vol. 1, eds. J. DeBoer and G. E. Uhlenbeck (North-Holland, Amsterdam, 1962) p. 1; translated from N. N. Bogoliubov, J. Phys. (Moscow) 10 (1946) 256, 265.
4. E. G. D. Cohen, in: Transport Phenomena in Fluids, ed. H. J. M. Hanley (Dekker, New York, 1969) 157.
5. E. G. D. Cohen, in: Lectures in Theoretical Physics, Vol. 9C, ed. W. E. Brittin (Gordon and Breach, New York, 1967) 279.
6. E. G. D. Cohen, in: Fundamental Problems in Statistical Mechanics II, ed. E. G. D. Cohen (North-Holland, Amsterdam, 1968) 228.
7. M. H. Ernst, L. K. Haines, and J. R. Dorfman, Rev. Mod. Phys. 41 (1969) 296.
8. P. Résibois and M. De Leener, Classical Kinetic Theory of Fluids (Wiley, New York, 1977) Ch. 10.
9. P. Résibois, J. Stat. Phys. 19 (1978) 593.
10. J. Karkheck, H. van Beijeren, S. de Schepper, and G. Stell, Phys. Rev. A32 (1985) 2517.
11. D. C. Wallace, Phys. Rev. A35 (1987) 4334.
12. D. C. Wallace, Nonequilibrium Statistical Mechanics of a Dense Fluid II. The Theory without Momentum Correlations, Phys. Rev. A (submitted).
13. D. C. Wallace, J. Chem. Phys. 87 (1987) 2282.
14. D. C. Wallace, Phys. Lett. 122A (1987) 418.